UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION V

Date: August 18, 1994

Subject: Methodology for GC fingerprinting analysis
                Lenz Oil site, Lemont, Illinois

From: Mary Tierney, RPM

To: Lenz Oil Site File

A QAPP Amendment memo dated July 26, 1994, for the Lenz Oil site described additional RI/FS sampling of light non-aqueous phase liquids (NAPLs) and soils to be conducted at the site located in Lemont, Illinois. The amendment was prepared as a supplement to the RI/FS QAPP Addendum prepared by the Settling Respondents and approved by U.S. EPA on January 22, 1992.

Attached is the methodology that will be used to perform gas chromatography fingerprinting analyses on the NAPL samples. As explained in the July 26th Amendment, "because the results of the fingerprinting will be used only to determine whether different types of NAPLs are present at the site, the method does not require strict QA/QC procedures ". An example data sheet is also attached.

cc: George Schupp, QAS
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ENSECO PRODUCT SUMMARY
EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

This method is based on a methylene chloride extraction of a sample followed by capillary column gas chromatography with flame ionization detection. Extractable Petroleum Hydrocarbons are reported as Total Chromatographable Organics. Product identification (Diesel, Kerosene) are made if possible. The method is designed as a reliable alternative to EPA methods 413.1 and 418.1 which are susceptible to significant bias and use Freon 113 as an extraction solvent. This method is based in part on US EPA SW-846 Methods 8000, 8015, and 8100, plus ASTM D3328-78. It is similar to the California-LUFT DHS extraction procedure for diesel and to Method OA-2 as published by the University Hygienic Laboratory, Iowa City, Iowa.

Summary of Method

Extraction

Samples are spiked with a surrogate (ortho-terphenyl) and extracted with methylene chloride and concentrated to 1 mL. Sample sizes are 1 L for waters, 25 grams for soils, and 1 gram for wastes. Water samples are extracted with Method 3510 or 3520, and solid samples are extracted with Method 3540 or 3550. (Freon is not used as an extraction solvent due to environmental concerns associated with this solvent. In addition, some studies indicate improved recoveries with a more polar solvent such as methylene chloride.)

GC Analysis

Samples are analyzed on a 30 meter narrow bore fused silica capillary column. The column allows for the resolution of n-alkanes from n-C8 to n-C32, as well as the resolution of phytane/n-C18 and pristane/n-C17. The method's linearity is demonstrated by a multi-point calibration of a multiple component hydrocarbon mixture; and calculations are corrected for the response of an internal standard, 5a-androstane.

Quantification

Sample results are based on the total chromatographic area between n-C8 and n-C32 using the response factor for ortho-terphenyl rather than individual products. Ortho-terphenyl has an equivalent response to eicosane (n-C20), and, in turn, eicosane has a similar response to other hydrocarbons between n-C8 and n-C32. This quantification technique eliminates the variability inherent in the use of local products for calibration, but yields a calibration bias for typical unweathered fuels. (Calibration bias is the ratio of the calculated amount to the actual amount.) For example, kerosene, diesel #2, and fuel oil #2 have a bias of approximately 1.0. In other words, calibration by this technique is equivalent to calibration with a product like diesel #2 or kerosene. Other products like gasoline and motor oil have a lower bias of approximately 0.50 because some components of these products are either too light (gasoline) or too heavy (motor oil) to be chromatographed under the analytical conditions of this method.

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Another important aspect of the quantification is the inclusion of total resolved and unresolved area by forcing a horizontal baseline across the chromatogram. A blank correction is performed to eliminate baseline elevation due to column bleed. This approach is more accurate across a calibration range of a product like diesel than a simple summation of valley to valley integrated peaks. It is also a more accurate measurement of environmentally weathered products.

In addition to functioning as the calibration standard, ortho-terphenyl is used as the surrogate standard. It is spiked into each sample to provide an evaluation of recovery for each sample. This recovery may be affected by matrix interference or sample dilution.

The reporting limit based on diesel #2/fuel oil #2 is 0.1 mg/L for water and 4 mg/kg for soil.

Identification

The composition of various petroleum products may vary depending on refinery operation, seasonal additives, and crude oil sources. As such, identification of products, especially weathered products, can be very complicated. If a match can be determined, the following products can be identified:

Gasoline
Aviation Gasoline
Kerosene and Jet Fuel A
Paint Thinner
Turpentine
Fuel Oil #2 and Diesel #2
Fuel Oil #4
Fuel Oil #6
Coal Tar
Creosote
Lubricating Oils
Processing Oils
Vegetation Hydrocarbons
Asphalt

Additional information, such as, distribution ranges based on n-alkanes, degree of weathering based on pristane/c-C17 and phytane/n-C18 ratios, concentration of n-alkanes and ratio of resolved to unresolved can be provided on request. If standards are available, specific products can be identified using pattern matching as described in ASTM D3328-78.

Quality Control

Duplicate laboratory control spikes of fuel oil #2 are analyzed every 20 samples. A method blank containing ortho-terphenyl as a surrogate spike is analyzed with each batch. The blank amount should be less than the method reporting limit. In addition, each sample is spiked with the surrogate (ortho-terphenyl) to monitor extraction efficiency. Matrix spikes, duplicates and field blanks are recommended as necessary to satisfy data quality objectives.

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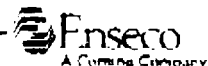
Example Datasheet:

EXTRACTABLE PETROLEUM HYDROCARBONS
GC/FID

Client Name:
Client ID:
Lab ID:
Matrix: Soil   Sampled: 27 MAR 90   Received: 27 MAR 90
Authorized: 28 MAR 90   Prepared: 10 APR 90   Analyzed: 12 APR 90

Parameter	Result	Units	Reporting Limit	
Total Chromatographable Organics	50	mg/kg	4	1
Surrogate	Recovery			
O-Terphenyl	85	%	--	

Note 1:   Qualitative Identification: This sample has GC/FID characteristics
          That are similar to Diesel Fuel/Fuel Oil #2. The sample resembles a
          hydrocarbon product occurring within the n-alkane range of C7 to C29.

ND = Not Detected

Reported by: Approved by: